WATER AND ATRAZINE MOVEMENT IN A CALCAREOUS COMPOST APPLIED SOIL DURING SIMULATED MULTIPLE STORMS EVENTS

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Abstract. The retention and movement of water and atrazine (2-chloro-4-ethylamino-6isopropylamino-s-triazine) was investigated in a calcareous soil (Krome) amended with three types of compost: (1) Clean organic waste (COW)- municipal solid waste cleaned of plastic materials and metal containers, (2) Biosolids (BSD)- sludge from municipal waste and (3) Bedminster (BDM) - a mixture containing 75% COW and 25% BSD. The research was conducted in two phases; a columnleaching study (dynamic) and a batch-equilibrium method (static). The column study demonstrated that while applying simulated rain, atrazine, leached out at a slower rate by 41, 24, and 18% from soil amended with BDM, BSD, and COW composts, respectively, during the first simulated storm event. BDM application resulted in lowest water movement and atrazine-leaching rate compared to the other composts tested. This study suggests that adding 134 tha⁻¹ of compost to the calcareous soil increased soil water holding capacity, reduced water movement and increased atrazine detention and reduced leaching potential of atrazine thereby reducing the potential for groundwater pollution. This study further demonstrates that soil amendment (particularly BDM) is effective in reducing the leaching potential of atrazine at the low rainfall amounts (corresponding to 0.5 pore volume). However, such amendment may not be effective in preventing leaching under more intense rain conditions or multiple rainfall events (corresponding to 3 or more pore volumes).

Keywords: atrazine adsorption and desorption, compost amendments, leaching of atrazine, soil water content

1. Introduction

The agricultural area of South Miami-Dade County, Florida, is bound by urban development to the north, Biscayne Bay and Biscayne National Park to the east, Everglades National Park (ENP) to the west, and Florida Bay to the south. Agricultural production brings an approximate economic value of \$538 million annually to Miami-Dade County (Crane and Davis, 1988). Over 23,000 people are directly involved in the county's highly efficient agriculture. The climate is maritime subtropical with a yearly mean temperature of 23 °C and an annual rainfall of 165 cm.

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Mean annual relative humidity is about 62%. The warm climate, high humidity, and ample rainfall are appropriate for the production of tropical and subtropical fruits year round and traditional vegetable crops for eight months of the year. About 85% of precipitation occurs from June to September. The three main agricultural soil series in southern Miami-Dade County (Krome, Chekika, and Perrine) are calcareous and cover about 85% of the county's agricultural area. These soils overlay bedrock of porous limestone containing the shallow Biscayne Aquifer. The soils have low water holding capacity and high permeability (Savabi, 2001). Therefore, large quantities of water, fertilizers, and pesticides applied to crops during a growing season have the potential to leach into the aguifer. The recommended application rate of atrazine for sweet corn is about 3.0 kg ha⁻¹ in South Florida (Maynard and Olson, 2000). In 1996, the United States Environmental Protection Agency published an interim report on the South Florida Ecosystem Assessment documenting that nutrient and pesticide loading from agricultural and urban areas had significantly increased chemical concentrations in the water. The report highlighted that the nutrient-enriched waters from agricultural runoff affects the native vegetation of the ecosystem (USEPA, 1996).

Non-point source water pollution from agricultural operations is an important environmental issue. Atrazine had the highest detection levels among other pesticides found in surface waters and sediments of South Florida from November 1991 to June 1995 (Miles and Pfeuffer, 1997). Atrazine adsorption and desorption is highly dependent on many factors, such as soil water content, soil depth, organic matter, pH, clay mineralogy, and irrigation/precipitation. Atrazine adsorption is higher at a lower pH (Kalouskova, 1989; Wang et al., 1992; Weber, 1993). Soil organic matter plays a critical role in atrazine adsorption (Shea, 1989). Sorption of atrazine is high at pH < 6.7 when compared with sorption at higher pH levels greater than 7.4 (Madsen et al., 2000). Clay et al. (1995) reported that a combination of ammonia fertilizer and higher soil pH level increased atrazine movement through the soil. Shinde et al. (2001), investigated atrazine transport in three calcareous soils (Perrine, Krome and Chekika) of South Florida. They reported linear atrazine sorption isotherms for these soils and found that atrazine exhibited chemical non-equilibrium during transport under steady saturated water flow in Krome soil column.

Several studies demonstrated that amending soil with compost improves the soil's physical and chemical properties, microbial population density and enzyme activity, and crop yields (Pinamonti *et al.*, 1997; Parr and Hornick; 1992; Roe *et al.*, 1993). Maynard (1989) monitored nitrate concentration in the groundwater beneath plots receiving 112 tha⁻¹ of chicken manure compost, 112 tha⁻¹ mushroom compost, and control plots receiving 1.46 tha⁻¹ of 10-10-10 fertilizer. The study demonstrated that compost not only increased yields by providing nutrients to plants but modified the soil by increasing water holding capacity and organic matter content and reduced the potential for nitrogen leaching into the groundwater. However, the effect of composting on the retention of agri-chemicals and water has

been overshadowed by the possible adverse affect of trace metals (Nyamangara, 1998).

Agricultural soils in Miami-Dade County of south Florida are mainly composed of crushed limestone, which has a low water and chemical retention capacity, with a shallow depth. Therefore, sustaining a profitable agricultural system requires appropriate applications of fertilizers, pesticides and irrigation. Poor retention of water, nutrients and pesticides by these soils prompted this investigation into the use of compost as a soil amendment. Little information is available on organic pesticide retention by calcareous soils especially when subject to seasonally high rainfall. The objective of this study was to investigate the effects of different types of compost on soil water content and movement and leaching of an herbicide atrazine in a calcareous soil of south Florida under multiple storm situations.

2. Materials and Methods

2.1. EXPERIMENTAL SET UP

Soil from the Frog Pond area, near the city of Homestead and ENP, south Florida was used for this study. The soil series is Krome (loamy-skeletal, carbonatic, hyperthermic, Lithic udorthent) with an average depth of 20 cm. The most common cropping system in the Frog Pond area includes the rotation of sweet corn, tomato, beans, cucumbers and zucchini.

Three composts; (1) Bedminster (BDM) – a mixture containing 75% municipal solid wastes and 25% biosolids, (2) Biosolids (BSD)- sludge from municipal waste, and (3) Clean Organic Waste (COW)- municipal solid waste cleaned of plastics and metal container, commonly used in south Florida, were selected for this investigation. The control treatment was Frog Pond soil with no compost application (NOC). All composts were air dried to remove excess moisture. Each compost was applied at the rate of 1.1 kg per column on a air-dry weight basis. The chemical properties of the composts and soil are provided in Table I. Three replicate samples of soil with different compost mixture (1:1, 1:6 and 1:13; compost: soil) were analyzed for water content at zero, 33, and 1500 K Pa water potential. In addition, saturated hydraulic conductivity (Table II) was measured from each column with soil and soil-compost mixture using the falling head method (Klute and Dirksen, 1986).

2.2. ATRAZINE SORPTION STUDY

The distribution coefficient (K_f) for atrazine sorption was measured by batch equilibration method (Nkedi-Kizza et al., 1983). Soil and different individual compost material <2-mm in diameter were used for this study. A 20 ml atrazine solution with concentrations of 0, 1, 10, 15, 20 ppm in 0.01 M CaCl₂, was added to 1 g of oven-dried material. Triplicate samples were equilibrated for 24 h at ambient

TABLE I
Chemical properties (dry weight basis) of the composts: Bedminster (BDM), Biosolids (BSD), Clean Organic Waste (COW), and Frog Pond soil (FPS)

Properties	Unit	BDM	BSD	COW	FPS
Organic carbon	g kg ⁻¹	264	279	163	31
Total nitrogen	$\rm g~kg^{-1}$	18	41	12	3
Phosphate	$\rm g~kg^{-1}$	17	104	7	8
Potash	$\rm g~kg^{-1}$	4	1	0.12	1
Sulfur	$\rm g~kg^{-1}$	4.1	9	2	1
Magnesium	$\rm g~kg^{-1}$	4	6	3	2
Calcium	$\rm g~kg^{-1}$	37	72	124	360
Sodium	$\rm g~kg^{-1}$	1.6	0.3	0.3	0.4
Aluminum	$\rm g~kg^{-1}$	21.6	27.6	4.8	9.3
Boron	${\rm mg~kg^{-1}}$	22	15	22	14
Copper	${\rm mg~kg^{-1}}$	195	765	125	323
Iron	${ m mg~kg^{-1}}$	29655	18361	6638	6257
Manganese	${\rm mg~kg^{-1}}$	670	101	133	399
Zinc	${ m mg~kg^{-1}}$	707	1913	267	165
pH	_	6.7	5.8	7.1	7.3
Cation exchange capacity (NH ₄ Sat)	$C mol_c kg^{-1}$	22.8	33.7	19.0	6.1
Cadmium	${ m mg~kg^{-1}}$	4.9	5.7	1.5	1.1
Chromium	${\rm mg~kg^{-1}}$	64.0	40.2	36.4	56.1
Nickel	${ m mg~kg^{-1}}$	41.1	33.0	9.2	7.4
Lead	${\rm mg~kg^{-1}}$	131.0	72.1	86.0	18.8

 $\it Note.$ Analyses performed by A & L Southern Agricultural Laboratories, Inc., Pompano Beach, FL.

temperature (23 °C \pm 1 °C) on a linear shaker (38 mm stroke length, 180 strokes minute⁻¹). After equilibration, the suspensions were centrifuged at 7000 times gravity for 15 min, filtered through 0.45 μ m membrane filters, and then refrigerated at 4 °C until analysis. Atrazine concentrations in clear supernatant solutions were analyzed by HPLC-UV detection method (Nkedi-Kizza *et al.*, 1992).

The sorption coefficient for atrazine was determined by Freundlich nonlinear relationship (Travis and Etnier, 1981) given as:

$$S = K_f C^N \tag{1}$$

where S (mg g⁻¹) is the amount of atrazine adsorbed by the soil or composts at equilibrium, C (mg ml⁻¹) is the amount of chemical in solution at equilibrium, K_f (mg g⁻¹)(mg ml⁻¹)^{-N} is sorption coefficient and N is an empirical constant depending on the sorbate-sorbent interaction.

TABLE II Physical and hydraulic properties of the composts: Bedminster (BDM), Biosolids (BSD), Clean Organic Waste (COW), and Frog Pond soil (FPS)

Properties	Unit	BDM	BSD	COW	FPS
Saturated hydraulic conductivity	${ m mm~h^{-1}}$	39	32	34	42
Water content at saturation	%	55	53	58	50
Water holding capacity @ 1/3 bar	%	77	75	33	25
Water holding capacity @ 15 bar	%	45	57	31	8
Available water	%	32	18	2	17
Sand	%	_	_	_	60
Clay	%	_	_	_	12
Silt	%	_	_	_	28
Rock fragments	%	_	_	_	25

Note. Analyses performed by A & L Southern Agricultural Laboratories, Inc., Pompano, Beach, FL.

2.3. ATRAZINE AND BROMIDE TRANSPORT STUDY

A portable rainfall simulator was used to measure the leaching of atrazine from Frog Pond soil columns amended with different composts. The simulator consists of oscillating nozzles (VeeJet NO. 80100, Spraying Systems Co., Wheaton, IL), spaced 1.07 m apart (Foster et al., 1979), located 2.5 m above the soil columns, and mounted at an elevation of eight feet above the ground. The simulator was calibrated to simulate a uniform rainfall rate of 13 cm h^{-1} , highest rainfall intensity for south Florida based on 100 year return period. Rain gauges were used during the rainfall simulation to insure uniform distribution over the entire column set up. Grids constructed with $2'' \times 4''$ wooden planks were lined under the rainfall simulator (Figure 1). Each grid contained one PVC (polyvinyl chloride) pipe column, 57.15 cm in total height and 30.48 cm in diameter. Thirty cm of soil was packed over 25 cm of gravel in each column. Different composts were applied to the columns at the common application rate of 1.1 kg column⁻¹ (based on field rate of 134 tha⁻¹) on a air-dry weight basis. All columns were saturated from below, and then allowed to drain for two hours before starting of leaching experiment. Five storm events were then simulated during 4 consecutive days using a constant rainfall rate of 13 cm h⁻¹. Multiple storms were simulated to investigate how much leaching would occur in such an extreme scenario.

In addition to atrazine, bromide was employed as a non-adsorbent, conservative tracer to investigate the hydrodynamic character of the soil-compost medium. A 16.3 mg of Atrazine, equivalent to 3.0 kg ha⁻¹, was applied to each column. A 200 mg column⁻¹ of Br was used as a tracer. All chemicals were dissolved and mixed into 1000 ml of deionized water and sprayed on the surface of the column.

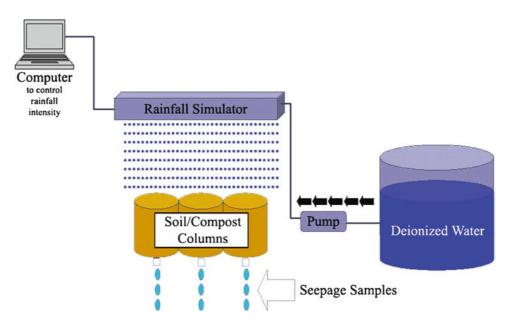


Figure 1. Field layout of columns and rainfall simulator.

The leaching study was conducted for a total of 13 h with 5 storm events of 2, 3, 2, 3, and 3 h durations. Effluent for Atrazine and Br breakthrough curves (BTCs) was collected for 5 s every 10 min based on a sample run on a similar column and manual help available. The total amounts were extrapolated from the point samples in time. The effluent sample was stored in 20 ml Teflon containers and placed in a freezer immediately after collection. Before analysis, the solution samples were filtered through 0.45 μ m membrane filters. Atrazine concentration in the column effluents was measured by HPLC-UV detection and Br concentration was measured by ion selective electrode.

At the end of experiment, soil samples from each column were collected to determine the residual atrazine concentration in the column. The column was divided into three sections; top, middle, and bottom, each 10 cm in depth. About 500 g soil was collected from each section. The samples were air-dried, ground, and sieved through a 2-mm sieve for total atrazine extraction. Extraction was performed using 5 g of soil from composite sample from each section (10 cm layer). The samples were mixed with 15 g of methanol solution, and equilibrated using the same procedure detailed for the adsorption study.

2.4. STATISTICAL ANALYSIS

A completely randomized design was used for the column experiment (four treatments with three replications). The data analyses were performed using Statistical Analysis System (SAS, 1999) by a two-way analysis of variance (ANOVA). Fisher's

Least Significant Difference (Sokal and Rohlf, 1995) was selected as a post hoc test to determine differences in treatments at $\alpha \leq 0.05$ level.

3. Results and Discussion

3.1. SOIL WATER RETENTION

The soil water at zero, 1/3 bar, and 15 bar potential were higher for the soil-compost mixture than soil alone (Table II). This result was expected because of the Krome soil particle size distribution. Krome soil is a coarse texture soil with about 25% rock fragments (>2 mm). The 1:13 soil to compost mixture corresponds to 134 t ha⁻¹ application rate of the compost, considering the 25 cm mixing layer.

3.2. Break through curves (BTCs) for bromide

The BTCs obtained from displacement of bromide solutions in the three compost amendments (BDM, BSD and COW) and with no-compost (NOC) as control are presented in Figure 2. The order of peak appearance with respect to pore volume (PV) was COW>BSD>NOC>BDM. This finding suggests that during our experiment the percolation rate was higher in COW columns than others. We found that the saturated hydraulic conductivity was the highest in the soils without compost (42 mm h^{-1} (± 6 mm h^{-1})) than in the soil-compost mixture (35 mm h^{-1} (± 4 mm h^{-1})). However, differences in the saturated hydraulic conductivity between soil and the soil-compost mixtures were not significant at probability level of $\alpha \leq 0.05$. Note that the experiment was not strictly conducted

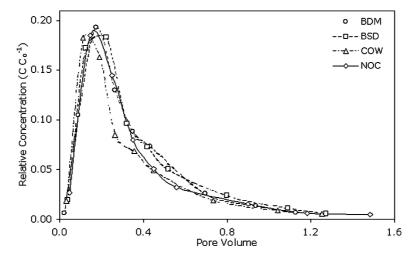


Figure 2. Bromide BTCs for BDM, BSD, COW and NOC.

under saturated water content conditions. As a whole, little difference in water movement characteristics among the three compost amendments and the non-amended Frog Pond soil was observed. However, BTCs indicated that bromide tended to leach slowest in BDM and fastest in the COW treatment. Note that BDM holds more water and COW least water (Table II).

Almost all bromide applied was leached out from the columns. The cumulative amount of bromide leached from 200 mg of Br applied per column at the end of experiment was used for statistical analysis. A one-way ANOVA to evaluate the effect of composting on seepage of water did not show significant differences ($\alpha \leq 0.05$ level) in the amount of Br leached from the four treatments.

3.3. SORPTION ISOTHERMS FOR ATRAZINE

Data from the sorption isotherms for atrazine are shown in Table III and Figure 3. Freundlich nonlinear adsorption isotherm (Equation (1)) was applied to the data. The values of K_f for the three compost materials and Frog Pond soil followed the order: BSD>BDM>COW>Frog Pond soil. A higher adsorption of atrazine was observed with composts than with Frog Pond soil. This is due to the presence of high concentrations of organic carbon (Table II) in the composts. The organic carbon content followed the order: BSD>BDM>COW>Frog Pond soil. Our results are in agreement with the finding by Laird *et al.* (1994), that soil organic matter has the highest adsorption affinity for atrazine among the soil constituents. The sorption

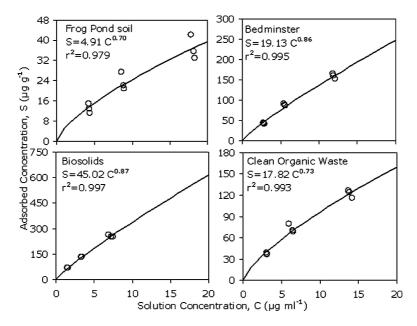


Figure 3. Atrazine adsorption isotherms for Frog Pond soil and different composts.

TABLE III Organic carbon (OC), adsorption coefficient (K_f , Equation (1)), correlation coefficient (r^2), empirical constant (N, Equation (1)) and K_{oc} for adsorption of atrazine for Frog Pond soil, and different composts without soil

OC (%)	K_f	N	r^2	Koc
3.1	4.9	0.70	0.97	114
26.4	19.1	0.86	0.99	63
27.9	45.0	0.87	0.99	153
16.3	17.8	0.73	0.99	99
	3.1 26.4 27.9	3.1 4.9 26.4 19.1 27.9 45.0	3.1 4.9 0.70 26.4 19.1 0.86 27.9 45.0 0.87	3.1 4.9 0.70 0.97 26.4 19.1 0.86 0.99 27.9 45.0 0.87 0.99

coefficient normalized to organic carbon content (K_{oc} , Table III) is within the range of values reported for atrazine of $K_{oc} = 100$ (Nkedi-Kizza et al., 1985). Although K_f values vary by a factor of about 10, the K_{oc} values are within a factor of 2.5 among soil amendments, which agree with findings of Nkedi-Kizza et al. (1983).

3.4. BTCs for atrazine

In Figure 4 the BTCs for atrazine during flow through columns with different compost applications are presented. The BTCs were asymmetrical in all cases. The cause of asymmetry is attributed to sorption kinetics for atrazine during leaching (Nkedi-Kizza et al., 1987, 1989). The peak concentration of the effluent decreases as the sorption coefficient (K_f) of atrazine increases for a particular compost (Table III). Similarly the area under the BTC at a given effluent volume decreases as sorption

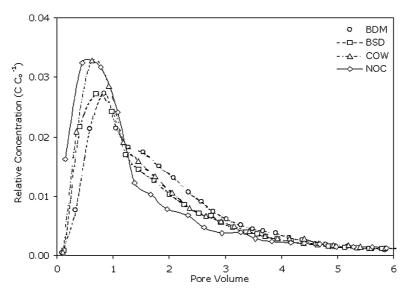


Figure 4. Atrazine BTCs for BDM, BSD, COW and NOC.

increases since the effluent concentration does not include the amount of atrazine adsorbed on the soil in the column. Although atrazine is more adsorbed in BSD compared to BDM, the peak of BDM appears later possibly due to less sorption kinetics. Atrazine BTCs from laboratory column studies show steep fronts and extensive tailing (Gaber *et al.*, 1995; Ma and Selim, 1994), especially with high water fluxes. Compost columns showed this extensive tailing behavior implying faster sorption kinetics. This tailing behavior means a long-lasting residual effect in the effluent. These results indicate that more atrazine is being retained in the columns compared to previously described bromide BTCs since atrazine leached significantly slower in all treatments. The order of retention of atrazine in the soil column and thus slower leaching follows the tenacity of sorption: BDM>BSD>COW>NOC. This result suggests that for the same amount of rainfall atrazine will leach faster in soil with no compost amendment (NOC) followed by soil amended with COW, BSD and BDM.

3.5. CUMULATIVE LEACHING OF ATRAZINE

The cumulative amount of atrazine in the effluent during leaching of the 16.3 mg atrazine column⁻¹ was used for statistical analysis (Figure 5). Atrazine leaching

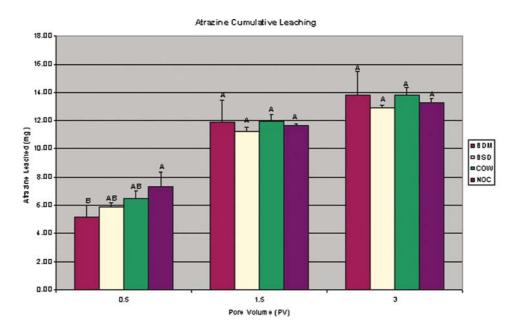


Figure 5. Cumulative leaching of atrazine recovered at different pore volumes (PV) of leachate from treatments which received 16.3 mg of atrazine each. The error bars represents the standard deviation of the mean. At each reported PV, values with the same letter do not differ significantly (Fisher's LSD, $\alpha \leq 0.05$).

from NOC did not differ significantly from leaching out of compost amendments anytime during the experiment. At the end of experiment all of the total cumulative amounts were similar to the atrazine applied. The results indicate that there was no initial atrazine in the composts and soil and about 78 to 87% of the applied atrazine was leached through the columns. The slight difference in cumulative amounts leached in the soil amendments as a function of total effluent could be attributed to differences in sorption kinetics in the different composts.

All the atrazine samples from soil extracts at the end of the leaching study were below the detection limit of <0.01 ppm. During the initial storm events (up to 2 PV, Figure 4), more atrazine leached out from NOC and higher amounts were retarded in the amended soil. Thus, composts amendments were effective in trapping atrazine and preventing it from leaching. However, when the columns were subjected to heavy multiple storm events, an extreme situation, subsequently the atrazine was flushed out.

4. Summary and Conclusions

The Frog Pond agricultural area near Everglades National Park, Florida, has been intensively used for vegetable and fruit production. The soil is made up of gravely limestone material with a shallow depth. A column leaching study was carried out to examine the effect of different composts on atrazine leaching during multiple storm events simulated under a rainfall simulator. Composting did help in increasing water retention and reducing percolation rate of Frog Pond rocky soil. Adding the equivalent of 134 tha⁻¹ of compost to the soil increased its atrazine trapping efficiency through increased sorption. It was confirmed that the Bedminster compost, with a slower percolation rate, detained the most atrazine. This study demonstrates that soil amendment (particularly BDM) is effective in reducing the leaching potential of atrazine at the low rainfall amount (corresponding to 0.5 pore volume). However, such amendment may not be effective in preventing leaching with more intense rains or multiple rainfall events (corresponding to 3 or more pore volumes). Based on the study results, we recommend that compost application may be considered as an alternative management practice to reduce the possible impact of farming on ground water quality in the region.

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